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AFRL-SR-AR-TR-03-

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0047

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE

12 Feb 03

3. REPORT TYPE AND DATES COVERED

FINAL REPORT

01 APR 99 TO 31 MAR 02

4. TITLE AND SUBTITLE

AB INITIO PROPAGATOR THEORY OF CLUSTERS

5. FUNDING NUMBERS

F49620-99-1-0185

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8. PERFORMING ORGANIZATION
REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

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4015 WILSON BLVD. ROOM 713
ARLINGTON, VA 22203-1954

10. SPONSORING/MONITORING
AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

APPROVE FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED

13. ABSTRACT (Maximum 200 words)

Oxidative processes involving aluminum lead to the creation of many intermediates whose structure and reactivity stimulate intense study. Aluminum-rich species are especially pertinent to the growth and structure of interfaces between bulk Al_2O_3 and metallic Al phases. Ceramics, minerals, reactive surfaces and catalytic supports often consist of oxides of aluminum. This project aims to improve understanding of the basic interactions between atoms of oxygen and aluminum at the atomic level. Quantum mechanical calculations on the structure and energetics of aluminum-oxygen clusters have been performed with methods that have predictive value for precise, spectroscopic experiments. The mathematical structure of the electronic structure methods employed also allows for qualitative interpretations in terms of the language of one-electron theory which nonetheless retain a rigorous connection to the correlated, ab initio theory that underlies the calculations. Methodological advances that allow consideration of larger and more complex clusters have been developed as well.

14. SUBJECT TERMS

20030306 053

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION
OF REPORT

UNCLAS

18. SECURITY CLASSIFICATION
OF THIS PAGE

UNCLAS

19. SECURITY CLASSIFICATION
OF ABSTRACT

UNCLAS

20. LIMITATION OF ABSTRACT

Final Report:
Ab Initio Propagator Theory of Clusters

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Grant Number F49620-02-1-0427-

99-1-0185

Objectives

Oxidative processes involving aluminum lead to the creation of many intermediates whose structure and reactivity stimulate intense study. Aluminum-rich species are especially pertinent to the growth and structure of interfaces between bulk Al_2O_3 and metallic Al phases. Ceramics, minerals, reactive surfaces and catalytic supports often consist of oxides of aluminum. This project aims to improve understanding of the basic interactions between atoms of oxygen and aluminum at the atomic level. Quantum mechanical calculations on the structure and energetics of aluminum-oxygen clusters have been performed with methods that have predictive value for precise, spectroscopic experiments. The mathematical structure of the electronic structure methods employed also allows for qualitative interpretations in terms of the language of one-electron theory which nonetheless retain a rigorous connection to the correlated, *ab initio* theory that underlies the calculations. Methodological advances that allow consideration of larger and more complex clusters have been developed as well.

Status of effort

Methodological developments have concentrated on the employment of generalized reference states in electron propagator calculations of electron binding energies. This project is motivated by the need for methods that are capable of treating large systems where a Hartree-Fock reference state is likely to encounter qualitative difficulties, thus preventing the use of traditional perturbative approximations appropriate for large molecules or renormalized, coupled-cluster reference states appropriate for small molecules. Time-resolved, photoelectron experiments on large, metal-oxygen clusters are likely to pertain to structures with one or more unpaired electrons and to reactivity where electron-pair bonds are stretched or broken. Photoionization experiments on metal oxide clusters that exhibit the enhanced reactivity of nanostructured materials aim to characterize the electronic structure of surface sites with dangling bonds or weakly paired electrons. New methods based on Kohn-

Sham reference determinants generated in density functional calculations show considerable promise for treating these kinds of situations. In addition, these methods will probably be useful for investigation of organometallics, large radicals and many other systems where the Kohn-Sham determinant offers a better description of a ground-state's electron density than a Hartree-Fock wavefunction.

Another development concerns the characterization of perturbative methods for electron affinities based on the highly successful P3 method for ionization energies for closed-shell molecules. Generalizations of these methods to open-shell species have been investigated as well. Computational tests of the P3 methods for ionization energies and electron affinities of closed and open shell systems have been undertaken and have established their efficiency and reliability [18].

Recently developed techniques have been used to investigate the electronic of small aluminum-oxygen clusters. Geometries, relative energies and electron detachment energies of anionic clusters have been determined. The results are in excellent agreement with experiments and indicate that the original structural proposals are incomplete or in error. From these findings, the role of isomerism in the spectra has been disclosed, the relationships between coordination environments and spectra have been established and the requirements for improved theoretical methodology can be inferred.

Accomplishments and New Findings

Aluminum Oxide Clusters

Photoelectron spectra of Al_3O_n^- clusters, where $n = 0 - 5$, were presented by Wang's group at several photon energies [1]. These workers investigated the sequential oxidation behavior of anion electron detachment energies and found that, as n increases, electron affinities of the neutral clusters grow. With changes in ion source and carrier gas conditions, the relative intensities of prominent spectral features change. This effect implies the presence of more

than one isomer in each mass-selected, anion photoelectron spectrum.

In our study of these assignment problems, the most stable anionic structures from density functional calculations were reexamined with additional geometry optimizations at the QCISD level [2]. QCISD geometries were used in subsequent electron propagator [3] calculations of the vertical electron detachment energies (VEDEs) of the anions. Two recently developed approximations in electron propagator theory were used here. The NR2 method is suitable for calculating the lowest electron detachment energies of closed-shell species [4]. For ionization energies of typical closed-shell molecules below 20 eV, the average absolute error is less than 0.2 eV. If a molecule is suspected of having significant biradical character, or if an anion has a concentrated negative charge distribution, the BD-T1 method may be employed [5]. Here, a Brueckner doubles, coupled-cluster reference state is adopted and the full set of couplings among simple field operators and triple field operator products (except for 2ph-2hp couplings) is calculated.

Al_3O and Al_3O^-

Hartree-Fock and perturbative calculations on Al_3O encountered a $^2\text{B}_2$, T-shaped minimum and a $^2\text{A}_1$, Y-shaped transition state within 1 kcal/mol of each other [6]. A detailed examination of Al_3O and Al_3O^- potential energy surfaces near the D_{3h} structure considered the importance of strong correlation effects pertaining to Jahn-Teller distortions [7]. Wavefunctions at C_{2v} minima for $^2\text{B}_2$ Al_3O and $^1\text{A}_1$ Al_3O^- each were dominated by a single configuration. A D_{3h} $^3\text{A}_2'$ structure for Al_3O^- lay higher than the singlet. To interpret anion photoelectron spectra, configuration interaction (CI) calculations were performed on Al_3O at both anionic structures. The lowest electron detachment energies of the C_{2v} and D_{3h} isomers were ascribed to the two lowest peaks at 1.68 and 1.22 eV, respectively, in the experimental spectrum. Doublet excitation energies inferred from CI state energies were compared with spectral features at higher electron binding energies.

For Al_3O , there are two stable structures, with an energy difference of 14.5 kcal/mol. For

the anionic system, the structures pertain to different spin multiplicities (singlet and triplet). The ground state is a singlet and resembles structures obtained in previous studies [6, 7]. The singlet-triplet splitting is 5 kcal/mol and there is also another triplet at 10 kcal/mol above the singlet. Optimizations on the ${}^3A'_2$ anion with D_{3h} symmetry produced a total energy that is 0.20 eV above the lower C_{2v} triplet.

Calculations on electron binding energies provided an accurate assignment of all photoelectron peaks. Assignments were based on agreements within 0.1–0.2 eV between experimental peaks and computed values. Unexplained intensity ratios were explained by the near coincidence of two final states of the lower triplet isomer. The variability of the intensities was shown to be a consequence of the presence of more than one isomer.

In addition, Dyson orbitals provide simple explanations for changes in bond lengths from anionic to neutral species. Dyson orbitals also confirm simple electron counting rules based on a dianionic oxygen that leaves eight valence electrons for the aluminums. For Al_3O^- , six of the eight Al-centered electrons may be assigned to combinations of 3s-like hybrids. The two remaining electrons are assigned to multicentered, bonding orbitals.

Al_3O_2 and $Al_3O_2^-$

For the Al_3O_2 system, two different C_{2v} minima were found. For the anionic case, there are two structures with similar stability. Both are singlets and the energy difference between them is only 4 kcal/mole. A triplet planar structure is 28.0 kcal/mol higher in energy. For Al_3O_2 and $Al_3O_2^-$, there are stable D_{3h} structures which lie at 37.3 and 22.8 kcal/mol, respectively, above the minima. Planar structures are preferred over three-dimensional ones.

In the photoelectron spectrum of $Al_3O_2^-$ [1], the relative intensities of the peaks depend on the conditions of the anion source, especially the purity of the He carrier gas. Propagator calculations provide a complete assignment of the peaks and succeed in assigning some of the variable, less intense features to the less stable singlet anion.

Dyson orbitals provide qualitative interpretations of each photoelectron peak. A simple

pattern of localization applies to both singlet anions. By counting both O atoms as dianions, the Al atoms are left with six electrons which are distributed in the Al-dominated Dyson orbitals that correspond to the three lowest VEDEs. Higher VEDEs therefore pertain to Dyson orbitals that consist chiefly of O functions.

Al_3O_3 and Al_3O_3^-

For Al_3O_3 , two C_{2v} minima were found. The energy difference between the neutral structures is 11.5 kcal/mol. For the anionic system, there are two structures with similar stability. Both are singlets and the energy difference between them is 5 kcal/mol. The triplet planar structure is 15.4 kcal/mol higher in energy. For Al_3O_3 and Al_3O_3^- , there are stable three-dimensional structures which lie at 52.4 and 45.4 kcal/mol, respectively, above the respective, global minima. Once again, planar structures are preferred over three-dimensional ones.

In the photoelectron spectrum of Al_3O_3^- [1], intense peaks occur at 2.96 (X) and 3.7 (A) eV. Less intense features lie at 2.25 (X') and 5.2 (B) eV. The intensity of the X' feature is enhanced with higher laser fluence. This effect was attributed to photoisomerization. Propagator results indicate that the X and A peaks may be assigned to 2B_2 and 2A_1 final states of a box-like form of Al_3O_3 , respectively. Propagator calculations also show that a less stable kite-like form has three VEDEs that correspond to 2A_1 , 2B_2 and 2A_2 final states, respectively. NR2 and BD-T1 predictions are close to the X' peak. The 2B_2 and 2A_2 predictions correspond to the highly structured B feature.

After counting eight electrons for each oxygen dianion, four valence electrons remain for the aluminums. These electrons are described by two Al-centered Dyson orbitals in each isomer.

Al_3O_4 and Al_3O_4^-

Geometry optimizations on Al_3O_4 produce a three-dimensional structure with D_{3h} symmetry. There are, as with the previous case, two approximately isoenergetic singlets of the anion.

A low-lying triplet with D_{2d} symmetry was found as well. Distinct patterns of stability occur for the neutral and anionic minima which were discovered. For the anion, two planar structures are more stable than three-dimensional isomers. For the neutral, however, a pair of three-dimensional structures are clearly more stable than planar ones.

Electron propagator calculations on the vertical electron detachment energies of the two lowest anionic singlets are in close agreement with photoelectron spectra. Dyson orbitals corresponding to these energy differences may be concentrated on aluminum or oxygen atoms with low coordination number. In one isomer, the lowest vertical electron detachment energy pertains to an aluminum-centered Dyson orbital, whereas in the other case, the Dyson orbital for the lowest transition energy is concentrated on an oxygen atom with only one neighbor. The lowest triplet anion and two relatively unstable singlets may also contribute to the photoelectron spectrum. Investigation of complexes of the oxygen diatomic molecule and either of the two most stable isomers of $Al_3O_2^-$ indicates that their lowest vertical electron detachment energies coincide with low-energy features in the photoelectron spectrum whose intensity varies dramatically with photon energy and the conditions of ion production.

The relative stability of the anion and neutral structures may be explained by coulomb attractions and repulsions between aluminum and oxygen atoms. In the anions, aluminum atoms have smaller positive charges than in the neutrals and electrostatic attractions with negatively charged oxygens are weaker. In the neutrals, three-dimensional structures are favored, for the ions have higher coordination numbers. Planar structures have more atoms with low coordination numbers and are favored by the anions. The uncharged clusters therefore bear a closer resemblance to the three-dimensional structure of ionic bonds found in bulk phases. In the anions, separation of negative charges leads to a preference for planar geometries.

Al_3O_5 and Al_3O_5^-

For Al_3O_5 , there are two stable structures, with an energy difference of 10.0 kcal/mole. The ground state is a nonplanar structure with C_{2v} symmetry. For the anionic system, two different spin multiplicities (singlet and triplet) are considered. The ground state is a singlet and the singlet-triplet splitting is 27.5 kcal/mol. There are two stable singlet structures with an energy difference of 15.5 kcal/mole. The ground state has a planar C_{2v} structure that is similar to that of the second most stable neutral isomer. There is also a nonplanar structure at 20.1 kcal/mole that resembles the lowest neutral isomer. For Al_3O_5^- , a three-dimensional structure is preferred over planar ones; for the anionic system, planar structures are more stable than three-dimensional ones.

Four final states, 2B_2 , 2A_1 , 2B_1 and 2A_2 , contribute to the broad feature in the photoelectron spectrum. NR2 results predict a separation of only 0.2 eV between the lowest and highest members of this set. Considerable vibronic interaction may be expected in the final states and these effects may contribute to the breadth of the observed band.

Dyson orbitals for the first two electron detachment energies consist of 2p orbitals that are parallel to the nuclear plane on two terminal, exocyclic oxygens in antisymmetric (b_2) or symmetric (a_1) combination. Contributions from functions on other nuclei are negligible. The next two Dyson orbitals are similarly concentrated on the exocyclic oxygens, but the 2p orbital constituents are perpendicular to the nuclear plane. For the fifth and sixth final states, the dominant functions are still on the same nuclei, but the chief components are 2p orbitals that are aligned with the nearby Al-O bond axes. These results indicate that electron detachments occur with greatest ease from the oxygens with the lowest coordination number.

AlO_2 and AlO_2^-

For AlO_2^- , only one structure with $D_{\infty h}$ symmetry need be examined. In the photoelectron spectrum of AlO_2^- [8, 9], peaks occur at 4.23, 4.88 and 5.08 eV. NR2 results with the 6-

311+G(2df) basis at 4.15, 4.80 and 5.00 eV correspond to $^2\Pi_g$, $^2\Pi_u$ and $^2\Sigma_u$ final states, respectively. Dyson orbitals for the three electron detachment energies are dominated by oxygen functions.

Trends in Structure and Spectra

Close agreement between calculations and spectra and the rigorous association of Dyson orbitals with electron detachment energies allow some general conclusions to be drawn. Dyson orbitals are dominated by oxygen functions engaged in bonding interactions with aluminum functions or by aluminum functions with antibonding relationships to oxygen functions. In general, the number of final states corresponding to the former category corresponds to the number of electron pairs associated with dianionic oxides. The lowest electron detachment energies from this group have the smallest number of neighboring aluminum centers. The remaining final states are in the aluminum-dominated category. The lowest electron detachment energies from this group have the highest number of neighboring oxygen centers. While the oxygen-centered group generally exhibits higher electron detachment energies, there may be cases where a low-coordinate oxygen or group of oxygens may have a lower value than low-coordinate aluminums. An investigation of the photoelectron spectrum of a relatively difficult case, Al_3O_4^- , which is now in progress, shows that clusters with exocyclic chains may exhibit this kind of inversion.

Propagator Methodology

Kohn-Sham Reference States

Electron propagator theory has been applied successfully to the calculation of electron binding energies of not only atomic and molecular species, but also condensed matter systems. Many results have demonstrated the power of these methods in describing electron attachment and detachment processes beyond the Koopmans description. Among more recent methods based on Hartree-Fock reference states are the third order algebraic diagrammatic

construction (ADC(3)) [10] and the nondiagonal, renormalized, second-order (NR2) method [4]. These two approximations are more difficult computationally than KS methods, but both generally yield reliable information on electron binding energies with respect to ground state configurations. In solid state physics, a melding of DFT and EPT methodology has been used for some time. The GW approximation (GWA), where G means the Green's function and W stands for an effective interaction, was first proposed by Hedin in 1965 [11]. It has been employed over the past decade and has succeeded admirably in reproducing experimental results. This method features a simple expression for the self-energy operator, which allows the electron propagator of an interacting many electron system to be described in terms of another propagator of a virtual, non-interacting system with an effective potential.

We have recently derived a 2p-h Tamm-Dancoff approximation (2p-h TDA) using the Kohn-Sham determinant. By neglecting several terms appearing in the f_3 operator manifold (which comprises 2p-h and 2h-p operators), we obtained a simplified 2p-h TDA that is related to the GWA. Some numerical applications have been performed for the ionization potentials of small molecules. An especially promising approximation is based on the use of a simplified second-order self-energy expression which gives mean absolute errors that are comparable to those of the NR2 method.

P3 Quasiparticle Approximations

The diagonal, partial third-order (P3) approximation to the self-energy matrix has proven to be especially useful for ionization energies of large, closed-shell, organic molecules, for it represents a practical compromise of accuracy and computational efficiency without introduction of empirical parameters [12]. This method has been extended to electron affinities and to unrestricted Hartree-Fock reference states. Concepts which enable interpretation of P3 results include Dyson orbitals, pole strengths, relaxation self-energy terms and correlation self-energy terms. The capabilities of P3 models have been tested in calculations on atoms of the second, third and fourth periods and on electron binding energies from the G2

set of molecules and ions. Various basis sets and effective core potentials were tested. These results provide guidelines for effective employment of the diagonal, P3 approximations.

Personnel

The following persons have participated in these projects.

- V. G. Zakrzewski, staff member in the Chemistry Department at Kansas State University.
- Y. Shigeta, postdoctoral fellow.
- O. Dolgounitcheva, postdoctoral fellow.
- A. Mitin, postdoctoral fellow.
- A. Ferreira, postdoctoral fellow.
- G. Seabra, graduate student.
- B. Champion, undergraduate student.
- A. Martínez, faculty collaborator at National Autonomous University of Mexico in Mexico City.
- F. Tenorio, student collaborator at National Autonomous University of Mexico in Mexico City.

Publications

Several papers pertaining to this project have been produced [13, 14, 15, 16, 17, 18].

Meetings

Results pertaining to this project have been presented at the following scientific meetings.

- *Current Computational Capabilities of Electron Propagator Theory*, Pacifichem 2000, *Computational Quantum Chemistry: Theoretical and Experimental Perspectives*, International Chemical Congress of Pacific Basin Chemical Societies, Honolulu, Hawaii, December 17, 2000.
- *Electron Propagator Recipes for Computational Chemists*, 2001 Pan-American Workshop on Molecular and Materials Sciences: Theoretical and Computational Aspects, Gainesville, Florida, February 22, 2001.
- J.V. Ortiz*, *Electron Propagator Interpretations of Biradical Electronic Structure*, Sani-bel Symposia, Saint Augustine, Florida, March 1, 2001.
- *Interpreting Weak Covalent Interactions with Dyson Orbitals and Their Energies*, Symposium on Accurate Description of Low-Lying Molecular States and Potential Energy Surfaces, Division of Physical Chemistry and Subdivision of Theoretical Chemistry, American Chemical Society National Meeting, San Diego, California, April 2, 2001.
- *Electronic Structure of Aluminum Oxide Clusters*, Simposio Materia 2001, Instituto de Investigación en Materiales, Universidad Nacional Autónoma de México, Mexico City, Mexico, October 25, 2001.
- *Electron Binding Energies and Dyson Orbitals of Aluminum Oxide Clusters*, IX International Materials Research Congress, Cancún, Mexico, August 27, 2002.
- Estudio Teórico del Enlace Químico en Cúmulos de Aluminio y Oxígeno, CONAMET/SAM - Simposio Materia 2002, Santiago, Chile, November 14, 2002.

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